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The Effect of Starch on Clay Dispersions

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THE EFFECT OF STARCH ON CLAY DISPERSIONS

By: John L. Moore

Senior Thesis 470

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ABSTRACT

Cationic starches and anionic (oxidized) starches are compared in this thesis with respect to their effect upon dispersion. The methods used for determining dispersion quality were relative sediment volume (R S V) and the Hercules Hi-Shear Viscometer. These methods are compared as to their applicability for use as practical tools in determining color dispersion quality. Limitations of R S V are discussed with regard to clay-starch mixtures. Comparisons are made using both types of starch on predispersed and undispersed clays. Hercules rheograms are compared for samples using both starches and clays at 40 percent solids. The rheograms indicate no difference between the cationic and anionic using undispersed clay, however, the predispersed clay shows a slightly greater viscosity for the cationic as compared to the anionic.

INTRODUCTION

Today, more than ever, the paper industry is trying to produce better quality coated sheets at the same or lower price. The price and quality of casein plus the high cost of latex has forced the industry to make more use of starch as a binder, even though it is already the most heavily used.

Starch, however, is generally considered to have low pick resistance, to be hard to insolublize resulting in low wet rub, and due to greater amounts of adhesive necessary it reduces opacity.

In reports published (2 & 3) discussing cationic starches as coating adhesives, an increase in all properties mentioned above was reported. Preliminary investigation of cationic starches has indicated a definite attraction between the cationic portions of the starch chain and the negative fiber. Evidence (2) points to a definite chemical bond between these two charged particles.

If the positive ion of the starch molecule has such an effect upon the negative fiber it must in some way effect the clay particle which is believed to have a net negative charge. The primary purpose of this study then is to compare the effect upon dispersion of the cationic starch as compared to the anionic starch.

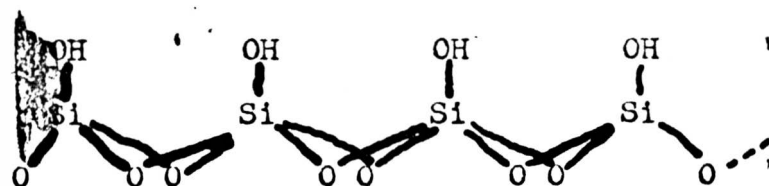
PROBLEM BACKGROUND

Much work has been done on the subject of clay dispersions for coating colors by Hemstock and Swanson (4), Asdell (1), Robinson (10), and Holtzman (5). Their theories of the ionic nature of dispersions are clear and well explained for many salts, acids, and bases used as dispersing agents. However, there was no record found of a comparison of cationic and anionic starches. To get a good background, the following subjects will be explored; clays, starches, and R S V.

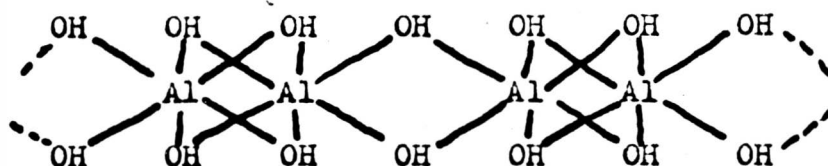
CLAY

Clay in the paper makers terminology refers to the hexagonal plate type of hydrous aluminum silicates called kaolinite. The plates are made up of layers of hydrated silica and Gibbsite.

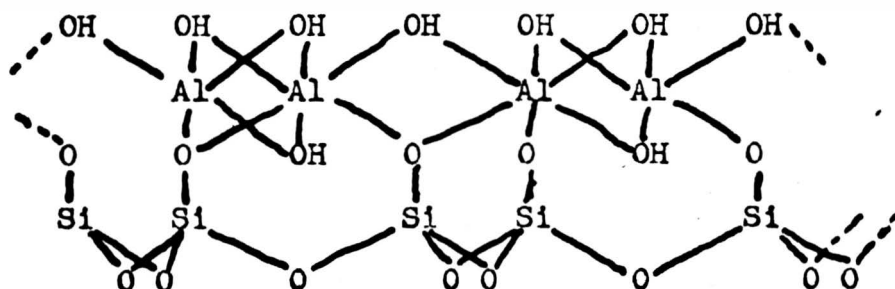
SILICA



GIBBSITE



KAOLINITE



This structure is essentially neutral although the edges do have areas where the structure can be broken leaving anionic and cationic active areas. The OH^- groups on the plate surface are available for hydrogen bonding. Bonds holding the kaolinite structure together are primary bonds. Those holding the kaolinite layers to one another are secondary. Thus splitting of the layers of a clay particle will not give rise to a charge. Only the edge wise fracture can do this.

The addition of H₂O to the kaolin gives us a complex system of secondary charges. Around the "active" edge areas, anions are preferentially adsorbed, in a simple system this could only be OH⁻ ion. On the surface, the OH⁻ groups of the kaolinite structure attract the OH⁻ ions of the surrounding media. These adsorbed ions carry with them water molecules of hydration. A water layer with a net negative charge is built up around the clay particle. This net negative charge will attract cations from the surrounding media. The cations will build up successive layers until the negative charge is neutralized. The degree of dispersion depends upon the pH and the nature of the cationic and anionic charges.

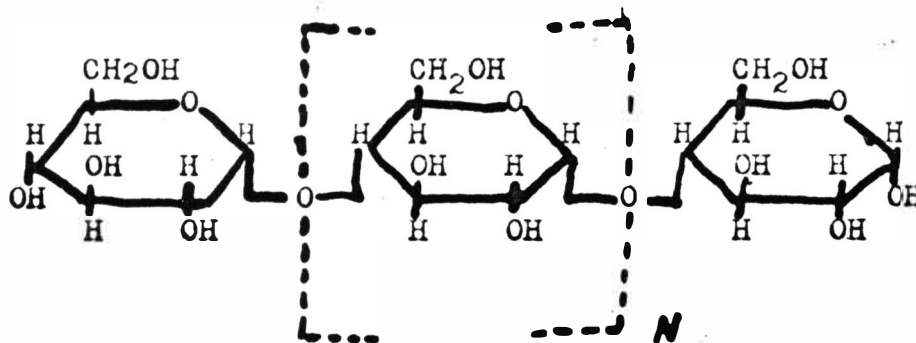
A smaller effect of H₂O in dispersing clay is the imbibition of water into the kaolinite structure. The kaolinite clays show swelling without detectable changes in the lattice (6). This adsorption of water will lower the specific gravity and reduce the force needed for dispersion.

STARCH

According to Morrison and Boyd (9), starch is a carbohydrate containing about 20% of a water-soluble fraction called amylose and 80% of a water-insoluble fraction called amylopectin. Both types are made up of glucosidic linkage. Amylose is a linear polymer and amylopectin is branched thru 1-6, - glucosidic linkages.

Natural starch has too great of a viscosity for use as a binding agent. Molecular weight of these large molecules is reduced by acid, oxidation, or enzyme conversion.

Starches can also be modified by substituting groups which contain a charge into the lattice. The amount and nature of these charges can be varied. This will give us a molecule which will have a different effect upon the clay than would a normal neutral starch.



STARCH CHAIN AND REPEATING UNIT

The starches to be used in this experiment will be an oxidized starch which is anionic in nature and a chemically modified cationic starch. It is expected that the anionic will give the better dispersing qualities, lower viscosity, and a lower binding strength than the cationic starch. Almost all coating starches are of the anionic nature, so much literature was available as to types, viscosity, strength, conversion, etc. The cationic starches for coating have never been used commercially, but Greif (2 and 3) studied and is doing further work in this area. He found the cationic starches gave much higher binding strength between fiber and clay particle. Higher viscosities and poorer dispersion than normal clays was also found at comparable percent starches.

MATERIALS

In coating applications, clay of an average particle size from .55 to 1.0 microns is used. In this work, an HT pulverized clay with 0.8 micron average particle size will be utilized. The clay will be free of impurities and deionized in an ion exchange resin.

Starches selected are derived from corn because of their wide use in the industry. The anionic starch will be a commercial grade oxidized with an 80-90 fluidity. The cationic starch should have the same fluidity and as small a positive charge as possible.

TESTING THEORY

The degree of dispersion of clay coating colors has been investigated by Robinson (10), Mattson, and Leighton (8). Robinson (10) derived on equation based upon the classical suspension viscosity relationship deduced by Einstein. This equation relates relative sediment volume to degree of dispersion.

$$S' V = 1$$

$$S' = \text{relative sediment volume} = \frac{\text{sediment volume}}{\text{volume of solids}}$$

$$V = \frac{\text{volume of solid}}{\text{vol. solid} + \text{vol. of liq.}}$$

His reason for the relationship is that if the particles are separate from each other, they will arrange to leave a minimum of empty space and sediment volume will be small. Furthermore, the process of dispersion of an agglomerated pigment may be considered to be the process of reduction of the sediment volume.

Mattson and Leighton used Robinson's theory and correlated viscosity to sediment volume by the equation given on the following page. As with Robinson's equation, all of the values needed can be

calculated from experimental data rather easily. The S term was found to depend upon the degree of dispersion as in Robinson's work and independent of solids, starch level, and type of starch used. The K (constant) was found to be dependent upon starch level and type of starch used and independent of the degree of dispersion.

$$N_{sp} = \frac{N - N_0}{N_0} = \frac{kV}{1 - SV}$$

N_{sp} = specific viscosity of the color

N_0 = viscosity of the adhesive in the total water present in the color

N = color viscosity

V = pigment volume per unit volume of color

S = a constant which is theoretically equivalent to the relative sediment volume of the dispersed pigment.

k = a constant which is characteristic of a particular suspension system.

By using the Mattson - Leighton equation and evaluating S and K using relative sediment volume and viscosity measurements, the degree of dispersion using the cationic and anionic starches can be determined.

PROCEDURE

The study of starch effects upon dispersion was to be made at coating solids and adhesive levels normally used in the paper industry (40-70 percent solids and up to 20 parts per hundred starch). All solids were checked by use of a moisture teller (Beckman).

-Clay- H. T. Predispersed (Minerals and Chemicals Phillips)
H. T. Lump (Undispersed) (Minerals and Chemicals Phillips)

Predispersed clays were prepared at 70 percent solids in a high speed mixer (Hamilton Beach) for a period of 30 minutes. The mixer capacity was 1000g clay-water slurry which was used in 200g samples.

Undispersed clay was prepared by mixing in a Read-Kneader for 3 hours at 80 percent solids. The clay was then diluted to 50 percent solids so it could be removed from the mixer. Even at 50 percent solids, it was very thick. Each batch yielded 3200g of clay slurry which was used in 200g samples.

-Starch- Stayco-M (anionic) (A. E. Staley Co.)
Cato-Kote #1448 (cationic) (National Starch Co.)

Hereafter the Stayco M shall be referred to as the "anionic" starch and Cato-Kote as the "cationic" starch. Also, parts starch per one hundred parts clay will be called parts per hundred (pph).

The "anionic" starch cook was made using 200g starch (dry) added to slightly over 800g water while cold to give a 20 percent solution after cooking since some moisture is lost during the cook. The cook was made in a 1.5 liter metal double boiler with constant stirring. The temperature of the starch was brought to $80 \pm 3^{\circ}\text{C}$ for 12 minutes.

The "cationic" starch cook was made under the same conditions as above. However, only half as much was made due to the limited quantity available. The cold starch solution was adjusted to a pH of 3.4 with acetic acid. The temperature was brought up to $80 \pm 3^{\circ}\text{C}$ and held for 25 minutes.

For all solids and starch levels, the amount of clay was held constant at 200g slurry. For predispersed clay this meant 140g and for undispersed clay 100g actual clay. After weighing out 200g solution, the amount of starch necessary to give the adhesive level (0, 5, 10, or 15 pph) was added. Next, water was added to obtain the proper percent solids. This was then checked with the moisture teller. The clay adhesive mixture was then mixed in a high speed mixer for 3-5 minutes. The only deviation from this procedure was the addition of cationic starch to 70 percent solids predispersed clay. This was done after the dilution water was added because of flocculation at high solids. The samples were adjusted to pH 7 to eliminate any effect of the low pH of the cationic starch.

The testing of samples was done according to the procedure below for R S V and the Hercules Hi-Shear Viscometer.

R S V

Part of each sample was put into graduated centrifuge tubes with the graduation marks perpendicular to the axis of rotation so that sediment volume could be read directly. The samples were then run at 2000 rpm for 1 hour. The total volume and sediment volume were recorded. Relative sediment volume was then calculated as shown in the theory section using slurry densities. The density of clay was taken as 2.58g/cm^3 .

Hercules Hi-Shear Viscometer

The rheogram for each sample was obtained by running the viscometer according to instructions issued with the machine. All samples used the "A" bob.

Data:

I. Hercules rheograms for all samples are given pages 13 thru 20.

II. Relative Sediment Volumes.

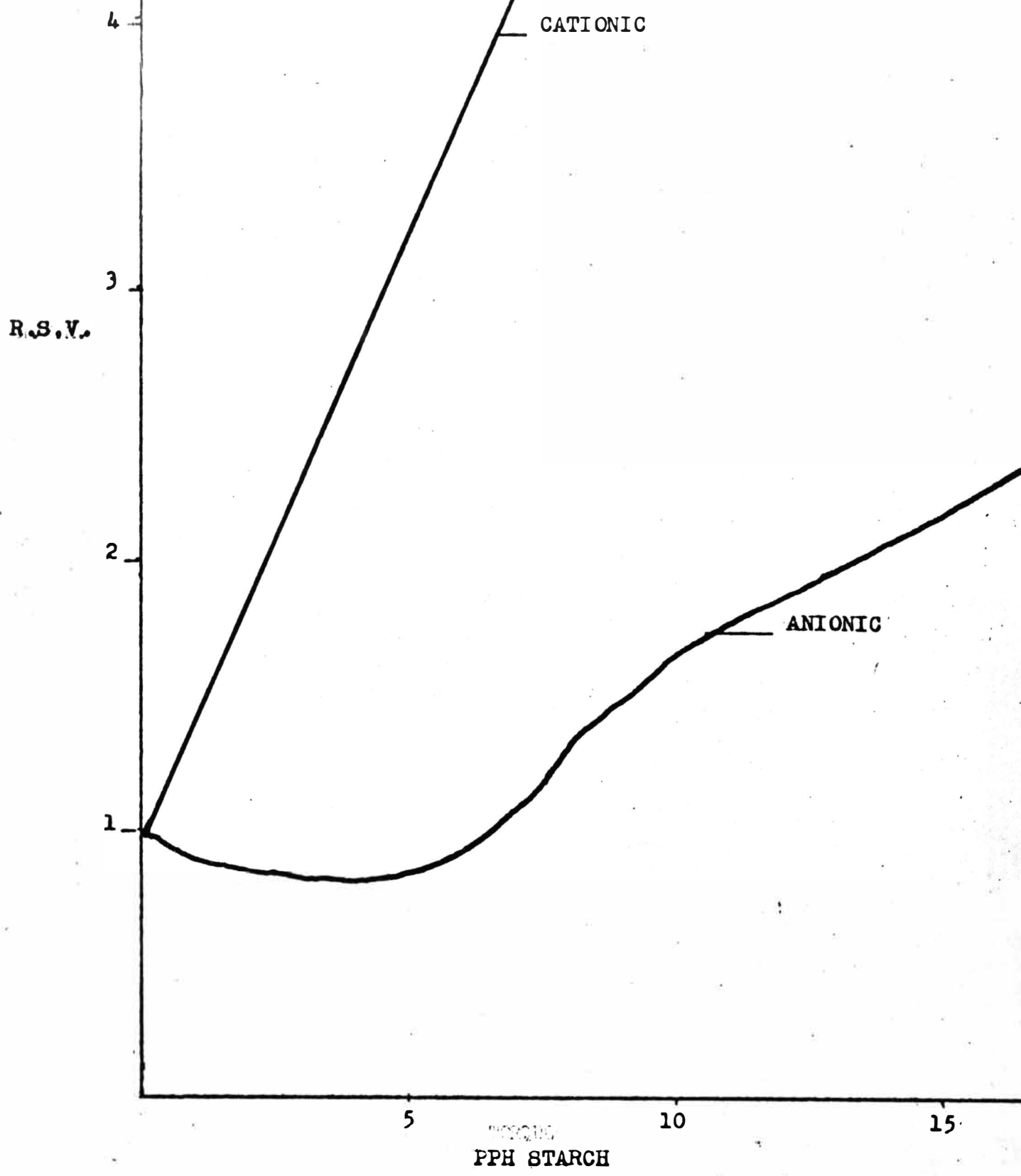
Table I - R S V at various starch levels for cationic and anionic starch using predispersed clay.

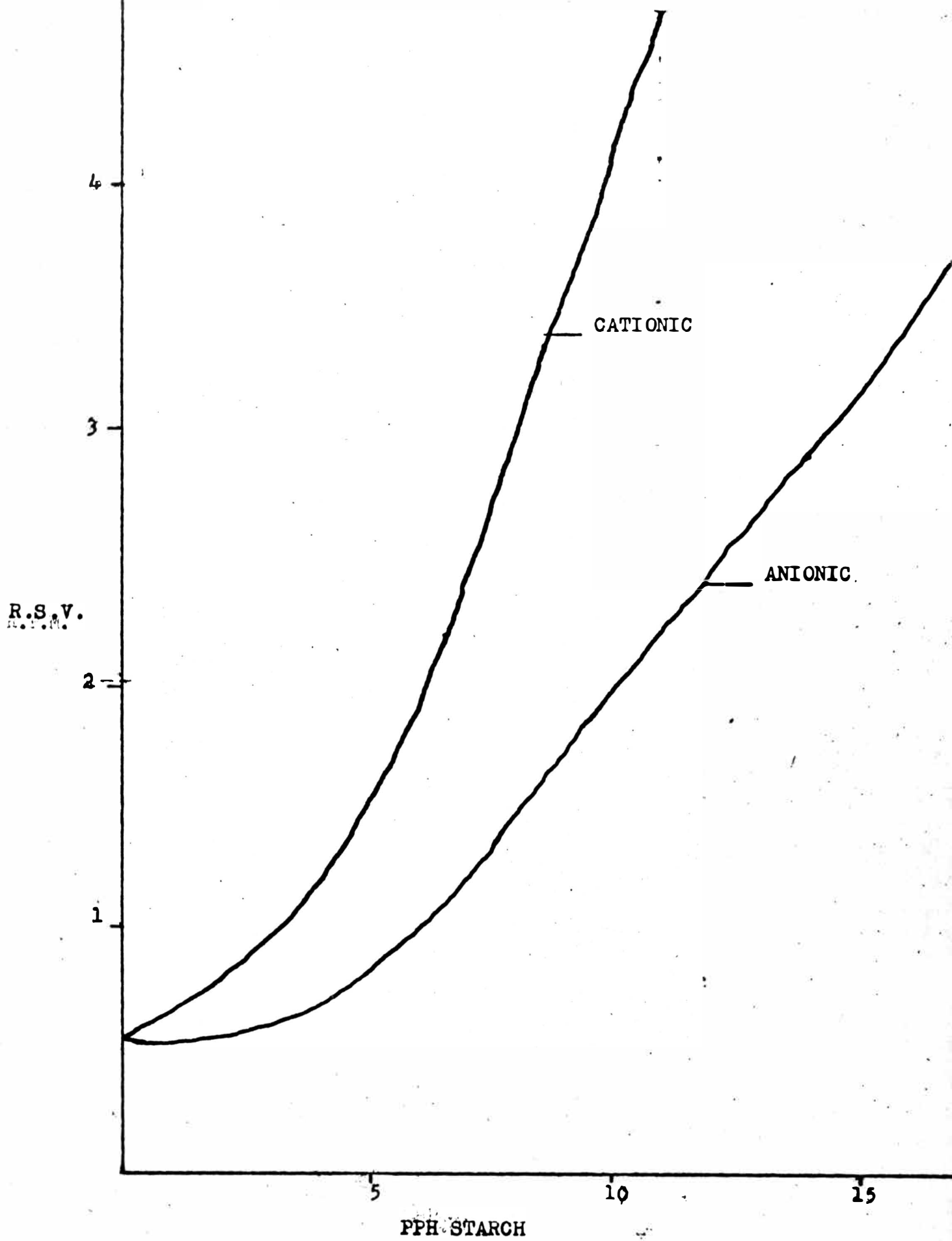
PPH	RSV			
	0	5	10	15
ANIONIC	2.53	2.34	2.88	3.04
CATIONIC	2.55	3.73	∞	∞

Table II - R S V at various starch levels for cationic and anionic starch using predispersed clay.

PPH	RSV			
	0	5	10	15
ANIONIC	2.79	2.93	3.44	4.11
CATIONIC	2.79	3.24	4.74	∞

∞ = No RSV





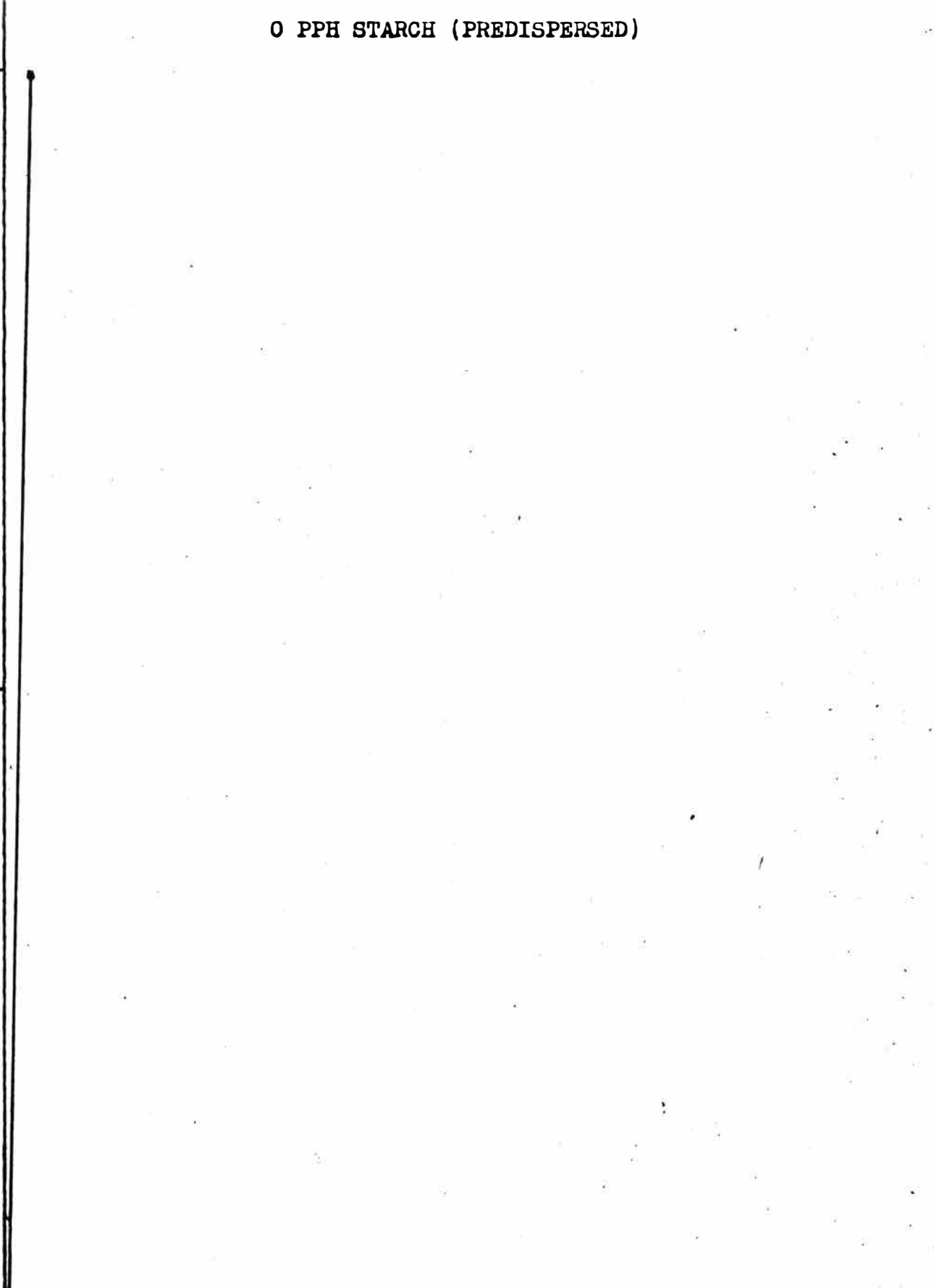
0 PPH STARCH (PREDISPERSED)

1000

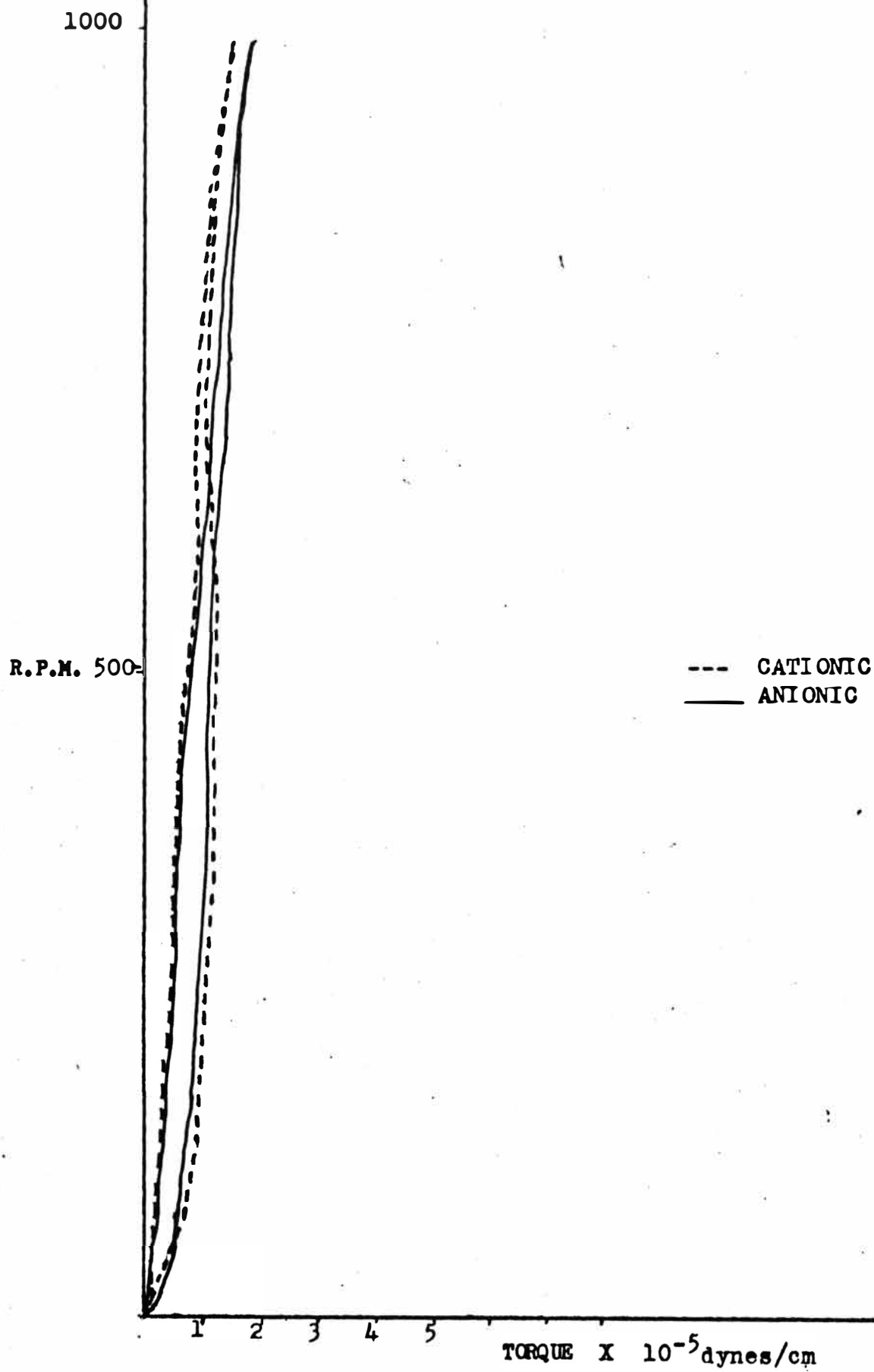
R.P.M.

500

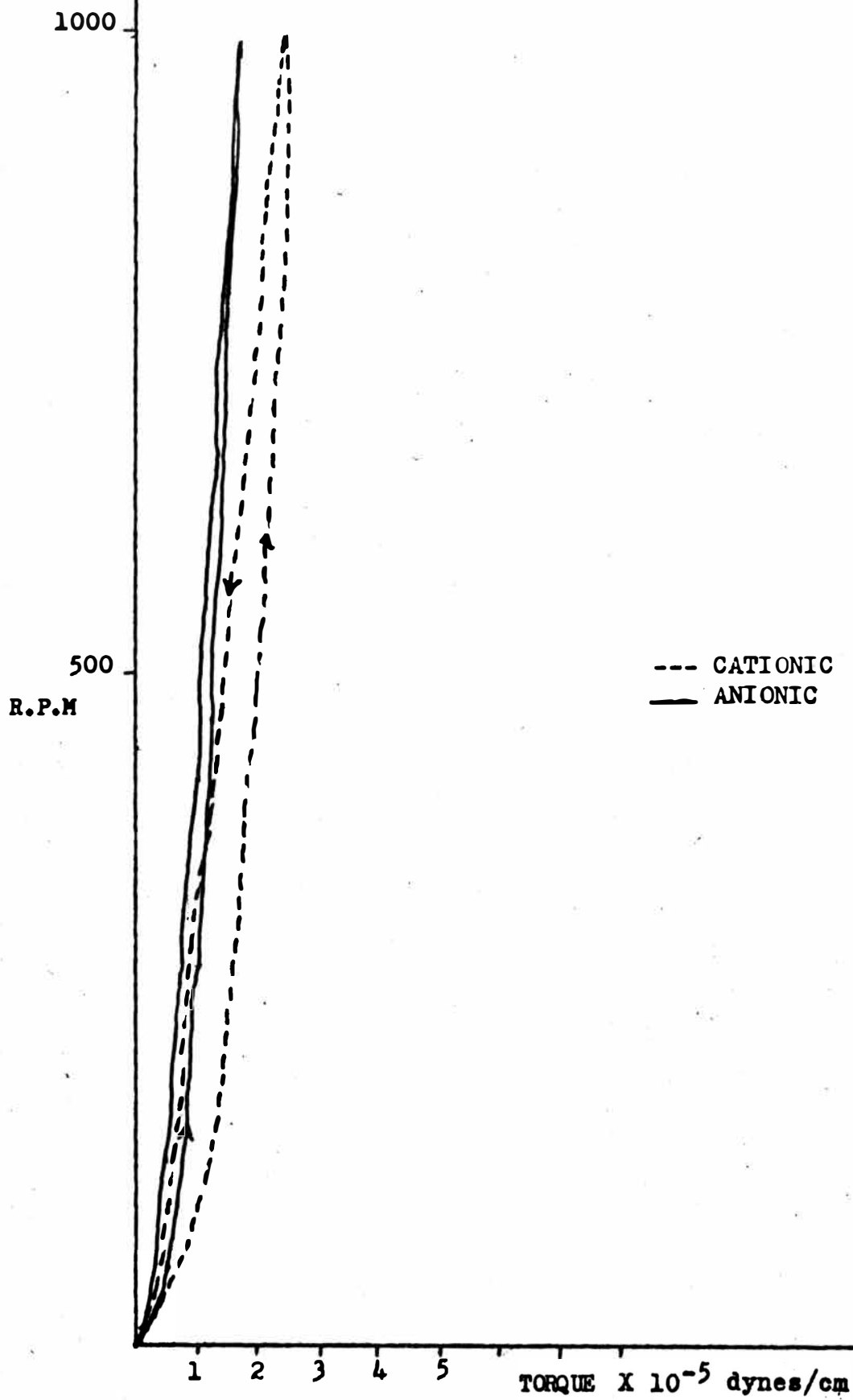
1 2 3 4 5 6 TORQUE X 10^{-5} dynes/cm



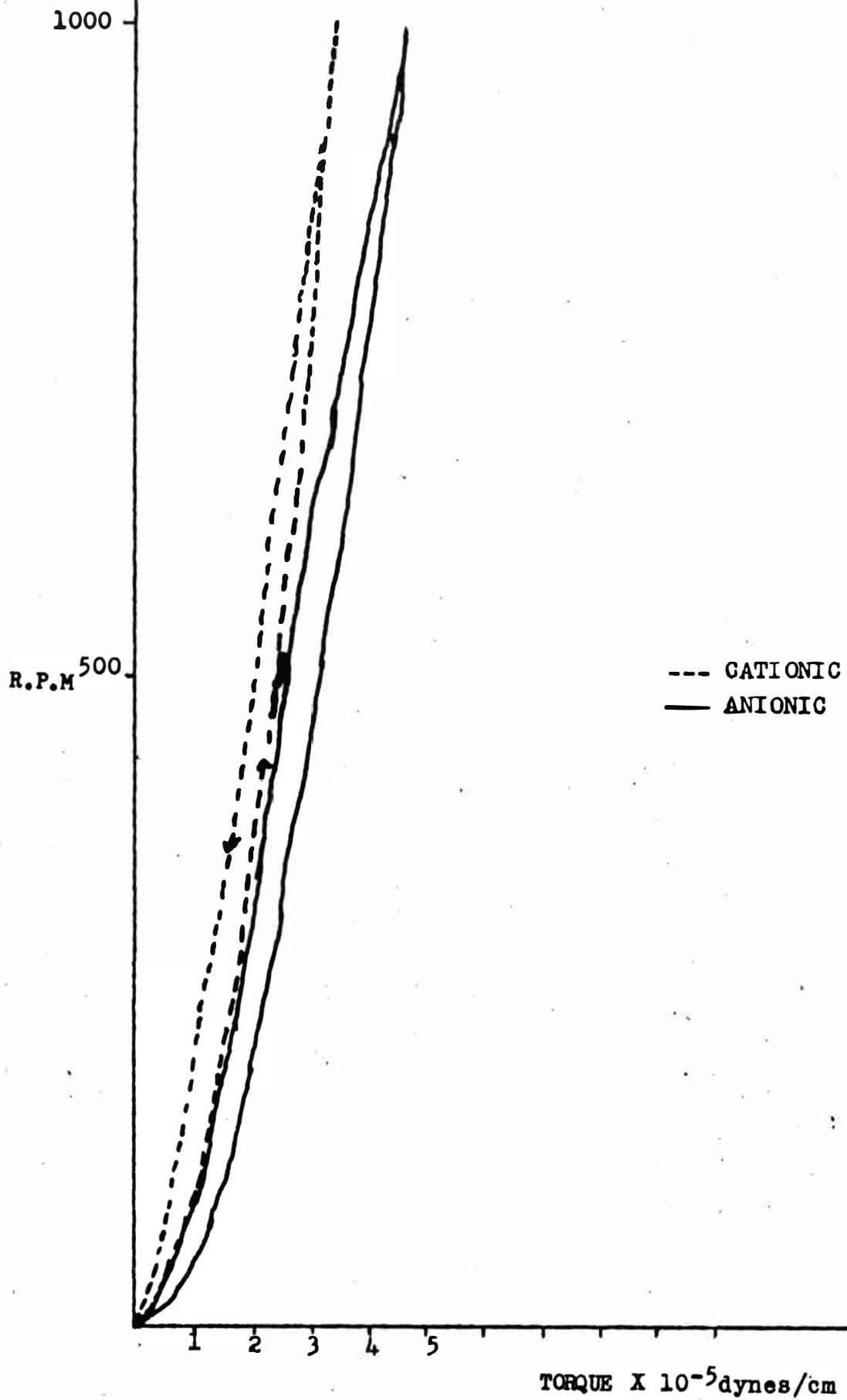
5 PPH STARCH (PREDISPERSED CLAY)



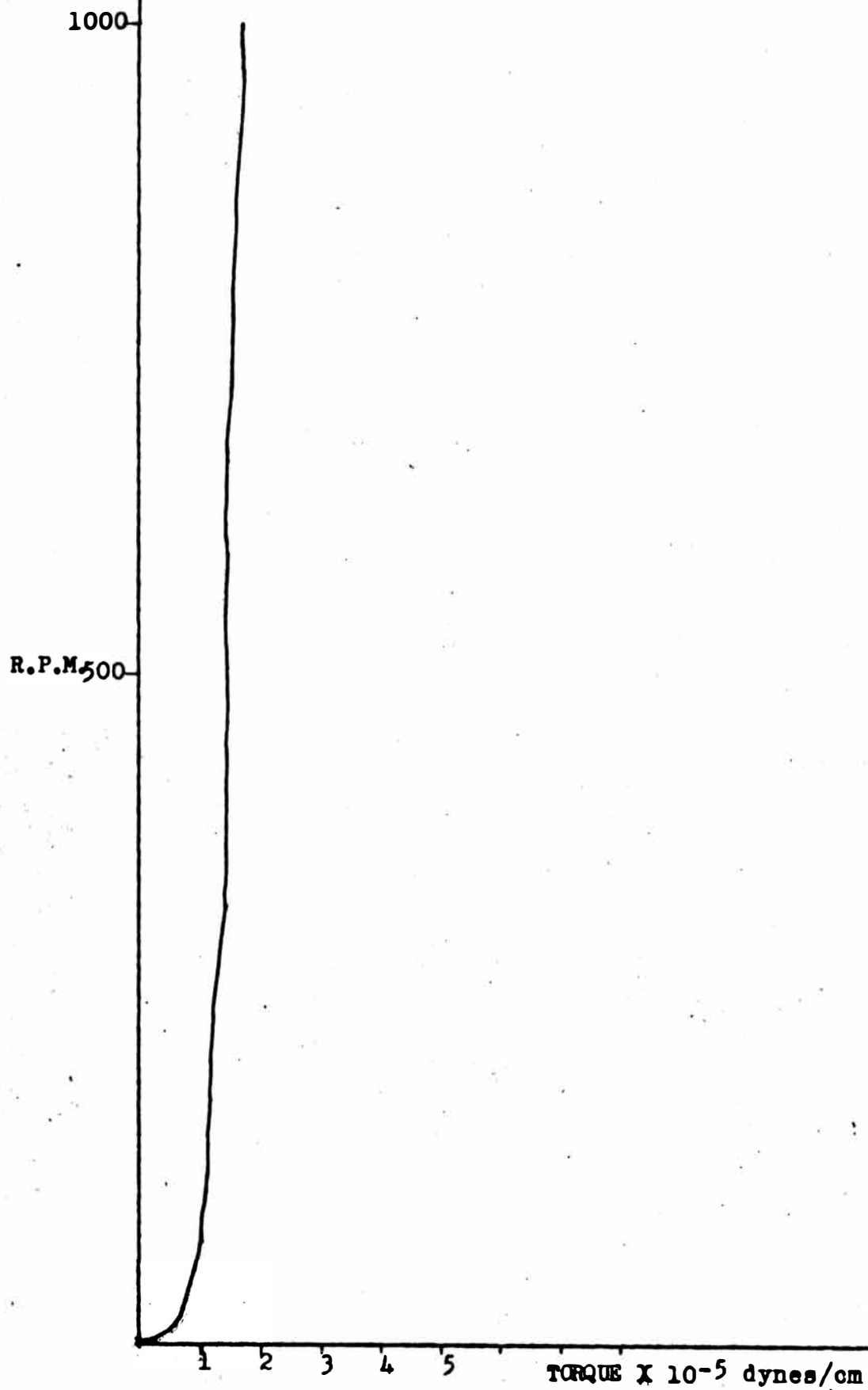
10 PPH STARCH (PREDISPERSED)



15 PPH STARCH (PREDISPERSED CLAY)



0 PPH STARCH (UNDISPERSED CLAY)



5 PPH STARCH (UNDISPERSED CLAY)

R.P.M.

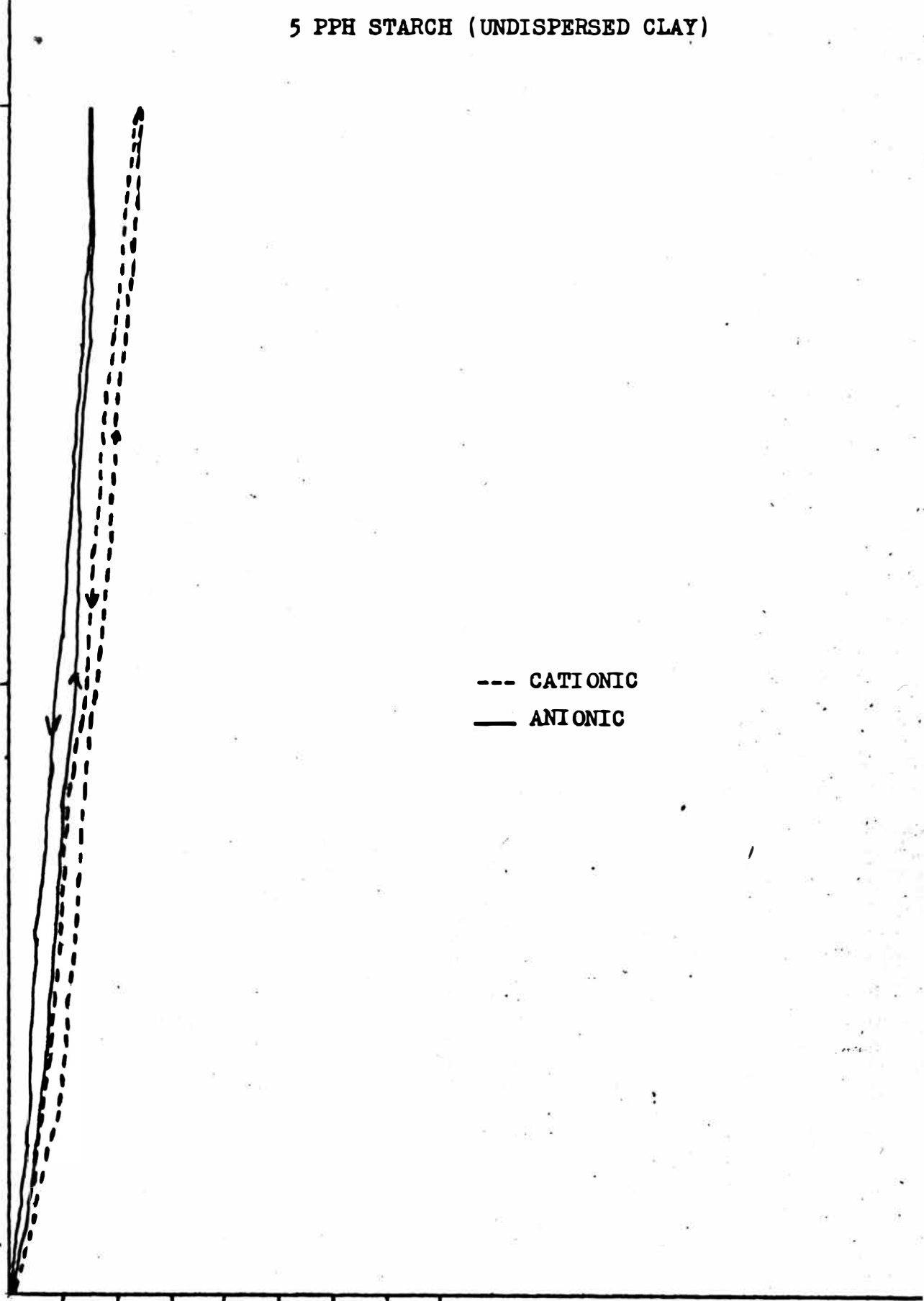
1000

500

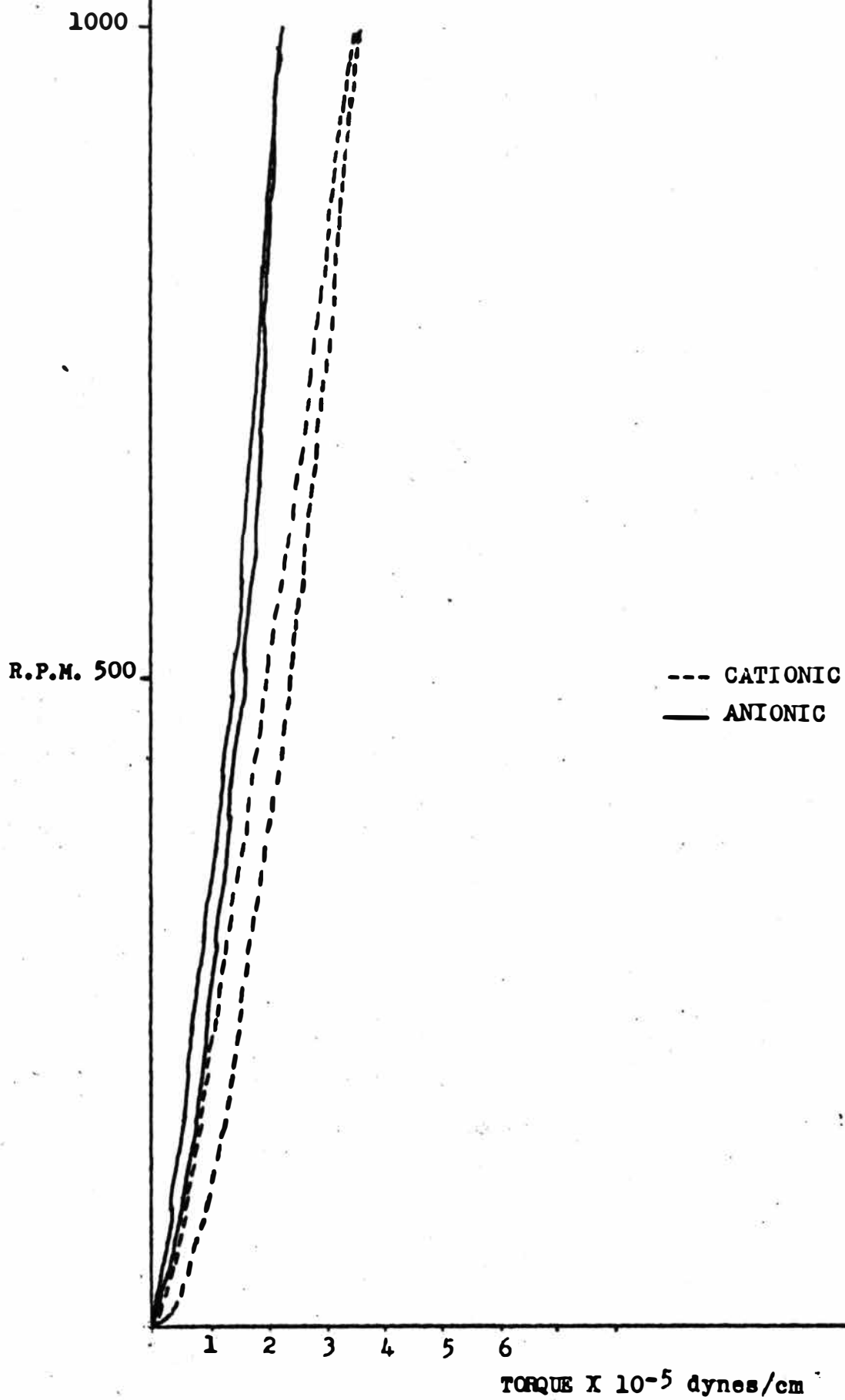
--- CATIONIC

— ANIONIC

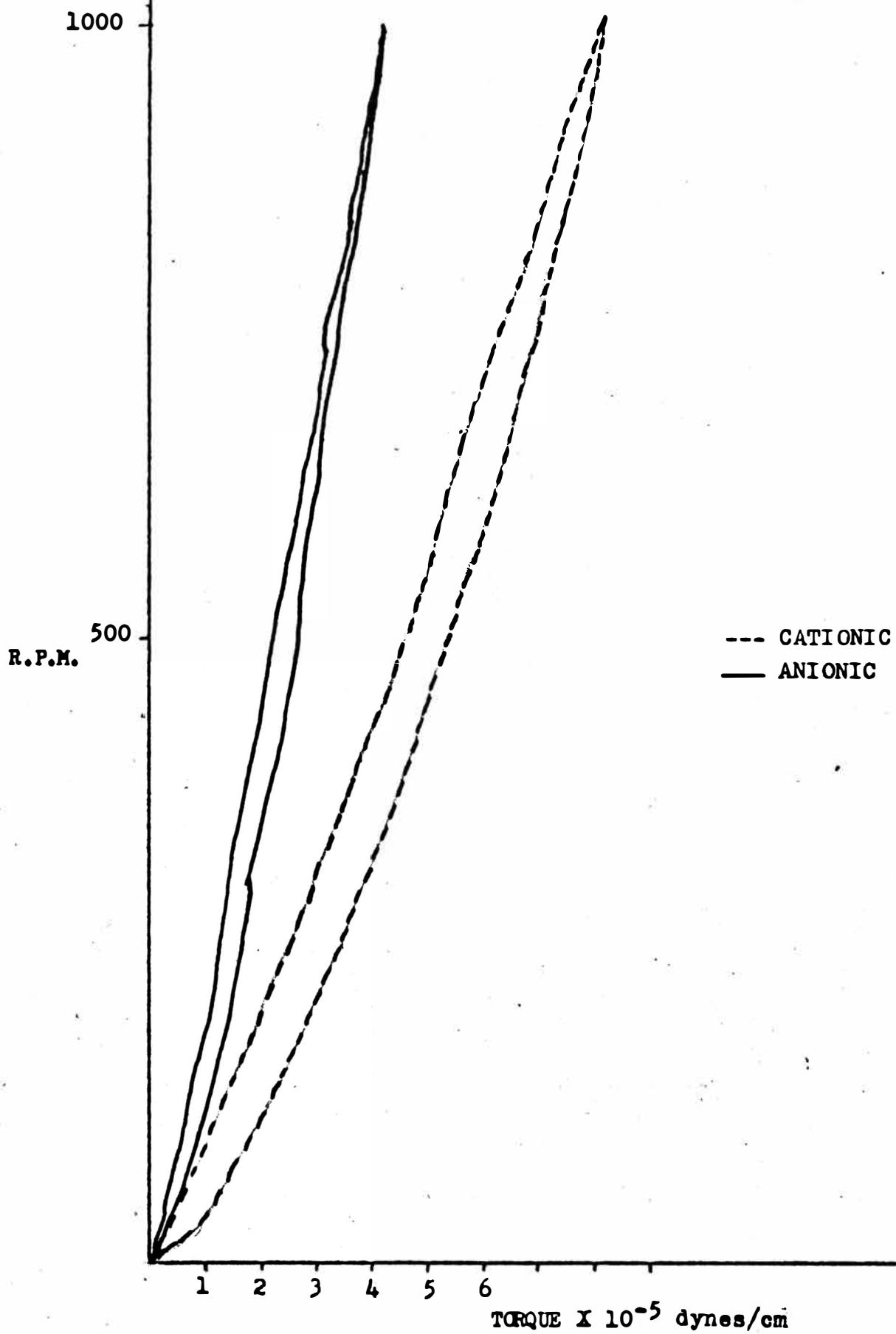
1 2 3 4 5 TORQUE X 10^{-5} dynes/cm



10 PPH STARCH (UNDISPERSED CLAY)



15 PPH STARCH (UNDISPERSED CLAY)



DISCUSSION OF RESULTS

Although it had been planned to use solids from 40 to 70 percent, all samples compared here are at 40 percent solids. Samples of even the best dispersed clay at 50 percent solids and above gave no sediment at starch levels greater than 5 pph. Thus, without a sediment, the effect upon dispersion for starch levels between 10-15 pph couldn't be observed. Many trials and times of centrifuging were tried but all yielded no conclusions from R S V.

At the solids level used in this study the Hercules Hi-Shear Viscometer does a very adequate job of showing the dispersion quality. Since R S V was to be the principle method, the solids level for this study was maintained at 40 percent. Even at this low solids level there was no sediment possible for the cationic starch at 10-15 pph. The former was true for both predispersed and undispersed clay. Forty percent was the minimum practical solid desired and as shown by figures 1 and 2, not much can be determined at higher starch levels. When these same samples are run on the Hercules, the rheograms didn't show a large difference in dispersion quality, which R S V for the same samples indicates. The cationic starch gave larger R S V's than the anionic starch at low adhesive levels and unmeasurable R S V's at higher levels.

Using undispersed clay, the cationic starch showed about 10 percent larger R S V's than the anionic at 5 pph, 40 percent greater at 10 pph and unmeasurable at 15 pph. This would indicate a large decrease in dispersion according to R S V concepts. For the same samples, rheograms shown in figures 3, 4, 5, and 6 show a minimum difference in color viscosity at all ranges. The Hercules rheograms are in agreement with personal observations which indicate a greater lowering (at low adhesive level) of viscosity with the cationic starch as compared to the

anionic. At higher adhesive level, both starches give identical viscosities.

The predispersed clay emphasized the difference between the two starches more than the undispersed clay. Only one sediment volume could be recorded which was at 5 pph and this was as high as 10 pph on the undispersed clay. R S V then would indicate that the cationic would give a much poorer dispersion than the anionic with greatly increased flocculation and viscosity.

Again, the rheograms from the Hercules Hi-Shear Viscometer didn't show this difference in the two colors. The rheograms show a slight increase in viscosity at 5 pph and larger increases at greater adhesive levels but still measurable and usable for comparisons.

CONCLUSIONS

Using undispersed clay, the cationic starch seems to show no undesirable dispersion effect. This could be due to a possible reverse counter-ion in which the large cationic groups form the adsorbed ion layer instead of anionic groups. The predispersed clay which is more practical as far as actual coating applications are concerned, shows that the cat-ion does cause some increase in flocculation and viscosity.

Further conclusions that can be drawn are that the Hercules must be considered a more reliable tool in predicting dispersion effects than R S V in the area of normal coating solids. R S V does a good job on clay-water systems but is overly sensitive or completely unusable in solids levels greater than 50 percent at adhesive levels greater than 5 pph.

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